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Note

Electron transfer. Part 165: Oxidations of Ti(II)(aq) with ligated iron(III) and ruthenium(III)

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Abstract

Titanium(II) solutions, prepared by dissolving titanium wire in triflic acid + HF, contain equimolar quantities of Ti(IV). Treatment of such solutions with excess Fe(III) or Ru(III) complexes yield Ti(IV), but reactions with Ti(II) in excess give Ti(III). Oxidations by $(NH_3)_5Ru(III)$ complexes, but not by Fe(III) species, are catalyzed by titanium(IV) and by fluoride. Stoichiometry is unchanged. The observed rate law for the Ru(III)–Ti(II)–Ti(IV) reactions in fluoride media points to competing reaction paths differing by a single F^-, with both routes involving a Ti(II)–Ti(IV) complex which is activated by deprotonation. It is suggested that coordination of Ti(IV) to Ti^{II}(aq) minimizes the mismatch of Jahn–Teller distortions which would be expected to lower the Ti(II,III) self-exchange rate.

Keywords: Electron transfer; Iron complexes; Ruthenium complexes; Titanium(II); Titanium(IV)

1. Introduction

Generation of aqueous titanium(II), as described by Kolle and Kolle [1] yielded solutions also containing equimolar quantities of Ti(IV) but which were unexpectedly easy to handle [2]. In contrast to earlier preparations reported by Olver and Ross [3] and Forbes and Hall [4], solutions 0.1 M in Ti(II) can be kept in triflic acid-HF media under argon for 12 h at room temperature.

Titanium(II) is a versatile reagent, but its action may be torpid. The difference in standard potentials (0.47 V) [3,5] documented for Ti(II) and Ti(III) corresponds, in the Marcus treatment for outer-sphere reductants [6], to a rate ratio exceeding 10^6. Observed rate differences for the two titanium reductants tend, however, to be much less marked, and in a few cases, Ti(III) reacts more rapidly [7].

The present report deals with the reductions, using Ti(II), of several mononuclear complexes of iron(III) and ruthenium(III). We seek mechanistic inferences concerning this novel reductant from changes in kinetic behavior resulting from variations in ligating species and reaction medium.

2. Experimental

2.1. Materials

Solutions were prepared from Millipore-Q-system deionized water that had been purged with pure argon for 2 h to remove dissolved oxygen. Titanium metal wire, ethanediaminetetraacetic acid iron(III) monosodium salt [NaFe(EDTA)], trifluoromethanesulfonic acid (triflic acid) and $TiCl_3$ solutions in HCl were Aldrich or Alfa products and were used as received. Titanium(II) solutions (0.10 M Ti^{II} in 2.0 M triflic acid) were prepared under argon by the method of Kolle and Kolle [2,7]; these green solutions were kept in sealed containers and used within 10 h of preparation.

Titanium(IV) solutions were prepared by air oxidation of Ti(II); after the oxidation was complete (as indicated by loss of color), argon was passed through the solution

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for 2 h to remove dissolved O_2. Preparation of Fe-(*o*-phen)$_3$(ClO$_4$)$_3$ utilized a modification of the method of Burstall [8], in which oxidation of the Fe(II) complex to Fe(III) was carried out with NaClO/HCl, rather than with Cl_2 [9]. Sodium triflate was prepared as described by Saha and Stanbury [10]. Ruthenium(III) complexes were prepared as their triflate salts by the method of Gaunder and Taube [11], as modified by Swavey et al. [12].

2.2. Stoichiometric studies

Stoichiometries of Fe(III)–Ti(II) reactions were determined by addition of measured deficiencies of Ti(II) to a known excess of Fe(III) at fixed acidity, waiting for 15 min intervals, adding excess NaI or KI solution, and then measuring the concentration of I_3^- formed (480–500 nm). Examination of the reactions with bound Fe(III) was carried out by measuring the decrease in absorbance of the oxidant at or near the low energy maximum: precipitation was encountered when $[Fe(CN)_6{}^{3-}]$ exceeded 1.0 mM and $[Ti^{II}]$ exceeded 0.6 mM. Stoichiometry of the Ti(II)–Ru(III) reactions was determined at the maximum of the highly colored Ru(II) product (550–620 nm). Results are summarized in Table 1.

2.3. Kinetic studies

Reactions were performed under argon and monitored at λ_{max} associated with the Fe(III) oxidant or the Ru(II) product, using a Durrum–Gibson stopped-flow spectrophotometer interfaced with an OLIS computer system. Temperatures were kept at 22.5 ± 0.5 °C. Ionic strength was maintained with CF_3SO_3H/CF_3SO_3Na. Reactions were most often carried out under pseudo-first order conditions with Ti(II) present in greater than tenfold excess and yielded exponential decay curves. The Fe^{III}(*o*-phen)$_3$-Ti^{II} reaction was rapid; even under second order conditions; only a lower limit for its rate constant could be obtained. Study of Fe^{3+}(aq) systems, with added halide or NCS^-, was complicated by ligation changes at the Fe(III) center on a time scale near to that for the redox reaction of interest.

Table 1
Reductions of Fe(III) and Ru(III) complexes using Ti(II): stoichiometries[a]

Oxidant	λ (nm)	[ox] (mM)	$[Ti^{II}]$ (mM)	Δ[Ox]/ Δ[Ti(II)]
Fe(III) (aq)	480, 500	5.0	1.0–2.0	1.92 ± 0.08
$FeCl^{2+} + FeCl_2{}^{+}$ [b]	480, 500	4.6	1.0–2.0	2.01 ± 0.10
$FeBr^{2+} + FeBr_2{}^{+}$ [b]	480, 500	4.6	1.0–2.0	1.96 ± 0.08
$FeF^{2+} + FeF_2{}^{+}$ [c]	480, 500	4.0	0.50–1.50	2.3 ± 0.1
$[Fe(CN)_6]^{3-}$	418	1.00	0.10–0.40	2.01 ± 0.09
$[Fe(EDTA)]^{-}$	340	1.00	0.10–0.30	2.03 ± 0.08
$[Fe(NCS)]^{2+}$ [d]	630	2.0	0.40–0.80	2.02 ± 0.11
$[Fe(o\text{-phen})_3]^{3+}$ [e]	555	0.50	0.10–0.20	2.23 ± 0.22
$Ru(NH_3)_5$-(4-AcPy)$^{3+}$	620	0.60	0.133–0.20	1.96 ± 0.01
$Ru(NH_3)_5$-(4-PyCONH$_2$)$^{3+}$	550	0.50	0.100–0.20	2.18 ± 0.03

[a] $[H^+] = 0.50$ M (CF_3SO_3H); $\mu = 0.50$ M unless otherwise noted. Results of studies at 480 and 500 nm were in agreement.

[b] $[H^+] = 0.50$ M, (CF_3SO_3H), $\mu = 2.5$ M (CF_3SO_3H + LiCl or NaBr). $[Hal^-] = 2.0$ M.

[c] $[H^+] = 0.50$ M (CF_3SO_3H); $\mu = 1.0$ M ($CF_3SO_3H + CF_3SO_3Na$ + NaF); $[F^-] = 0.25$ M.

[d] $[NCS^-] = 0.040$ M.

[e] $[H^+] = 1.75$ M (CF_3SO_3H); $\mu = 1.80$ M.

3. Results

Stoichiometric experiments (Table 1) with oxidants in excess indicate very nearly complete conversion to Ti(IV) in all systems chosen

$$Ti^{II} + 2Fe^{III} \rightarrow Ti^{IV} + 2Fe^{II} \qquad (1)$$

$$Ti^{II} + 2Ru^{III} \rightarrow Ti^{IV} + 2Ru^{II} \qquad (2)$$

Such reactions may be presumed to proceed through Ti(III). Kinetic profiles from the Ru(III) reactions and the faster Fe(III) reactions, carried out with Ti(II) in excess, (a total of 80 individual profiles embracing eight different systems) exhibit no irregularities pointing to the intervention of an intermediate formed or destroyed on a time scale comparable to that of the principal conversions. Reactions in this group then yield preponderantly Ti(III), in line with the lower reactivity of the trivalent state in a previous study [13].

Of the more rapid Ti(II)–Fe(III) systems, oxidation by Fe^{III}(EDTA) exhibits a straightforward monomial dependence

$$\text{rate} = k\text{Fe(EDTA)}^{+}][\text{Ti(II)}]; \quad k = (4.9 \pm 0.2) \times 10^3\ M^{-1}\ s^{-1} \qquad (3)$$

whereas reactions with $[Fe(CN)_6]^{3-}$ is strongly accelerated by H^+ (Table S1):

$$\text{rate} = [Fe(CN)_6^{3-}][\text{Ti(II)}](k_o + k_H[H^+]) \qquad (4)$$

$$k_o = (5.9 \pm 0.2) \times 10^4\ M^{-1}\ s^{-1};$$

$$k_H = (8.6 \pm 0.4) \times 10^4\ M^{-2}\ s^{-1}.$$

Table 2
Reductions of iron(III) complexes with Ti(II) and Ti(III): rate constants[a]

Oxidant	$k_{Ti(II)}$ ($M^{-1}\ s^{-1}$)	$k_{Ti(III)}$ ($M^{-1}\ s^{-1}$)
$[Fe(H_2O)_6]^{3+}$	$(4.2 \pm 0.4) \times 10^2$	$(1.7 \pm 0.2) \times 10^2$
$[Fe(EDTA)]^{+}$	$(4.9 \pm 0.2) \times 10^3$	$(3.2 \pm 0.3) \times 10^4$
$[Fe(CN)_6]^{3-}$	$(5.9 \pm 0.2) \times 10^4$ $+ (8.6 \pm 0.4) \times 10^4\ [H^+]$	$(1.7 \pm 0.2) \times 10^5$
$[Fe(o\text{-phen})_3]^{3+}$	$>1.5 \times 10^6$	2.6×10^5 [b]

[a] Reactions were run at 22.5 ± 0.5 °C; $\mu = 0.50$ M (CF_3SO_3H/CF_3SO_3Na) in most cases.

[b] 25 °C, $\mu = 1.0$ M (LiCl) (Akinyugha et al. Inorg. Chem. 17 (1978) 218).

Table 3
Kinetic parameters pertaining to reductions of substituted pyridine derivatives of $(NH_3)_5Ru(III)$[a]

Oxidant, $[Ru(NH_3)_5Lig]^{3+}$	K_{eq}[b]	$10^{-4}\ k_1\ (M^{-1}\ s^{-1})$	$10^{-7}\ k_2\ (M^{-2}\ s^{-1})$
Lig = 4-benzoylpyridine	104 ± 35	3.1 ± 0.1	2.8 ± 0.2
4-Pyridinecarboxamide	118 ± 38	2.4 ± 0.1	1.80 ± 0.11
4-Acetylpyridine	100 ± 22	3.1 ± 0.1	6.9 ± 0.6
3-Acetylpyridine	102 ± 19	2.4 ± 0.1	1.58 ± 0.09
Pyridine	114 ± 6	0.43 ± 0.01	0.43 ± 0.03

Rate = $-d[Ru^{III}]/dt = K_{eq}[Ru^{III}][Ti^{II}][Ti^{IV}][H^+]^{-1}\ (k_1 + k_2[F^-])$.

[a] Reactions at (22.5 ± 0.5) °C. $\mu = 0.50$ M ($CF_3SO_3H + CF_3SO_3Na$).

[b] Formation constant for $Ti^{II}Ti^{IV}(OH)$; $K_{eq} = \frac{[Ti^{II}Ti^{IV}(OH)]}{[Ti^{II}][Ti^{IV}][H^+]^{-1}}$.

For the most rapid oxidant examined. $[Fe(o\text{-phen})_3]^{3+}$, only a lower limit, $1.5 \times 10^6\ M^{-1}\ s^{-1}$ could be evaluated.

Rate laws and kinetic parameters for reductions of Fe(III) species by Ti(II) and Ti(III) are compared in Table 2. Note that these reactions are quite insensitive to added halide and Ti(IV).

In contrast, the reductions of Ru(III) derivatives of substituted pyridines (Tables S3–S7) are markedly accelerated by both added fluoride and added Ti(IV), with the Ti(IV)-dependence exhibiting kinetic saturation a high concentrations of this state (Table S2). Moreover, they are inhibited by increases in acidity. The fluoride dependences point to a kinetic contribution of a F^- containing path. At [Ti(IV)] well below the saturation region, reactions in this group proceed according to rate law (5)

$$\begin{aligned} \text{rate} &= -d[Ru^{III}]/dt \\ &= K[Ru^{III}][Ti^{II}][Ti^{IV}][H^+]^{-1}(k_1 + k_2[F^-]) \end{aligned} \tag{5}$$

where K pertains to the formation of a 1:1 Ti^{II}–Ti^{IV} complex, active in its deprotonated form. Calculated rates (in parantheses) are compared to observed values at the right of these tables. Rate and equilibrium constants obtained from refinement of the Ti(II)–Ru(III) data are collected in Table 3.

4. Discussion

Our experiments yield no evidence of inner-sphere paths in these reductions by Ti(II). The very rapid Fe(III) oxidants, $Fe(EDTA)^-$, $Fe(CN)_6{}^{3+}$, and $[Fe(o\text{-phen})_3]^{3+}$, are substitution-inert, and the most reactive of this trio, the phenanthroline derivative ($k > 10^6\ M^{-1}\ s^{-1}$) is devoid of bridging ligands. Its high reactivity may be reasonably attributed to a combination of its very positive oxidation potential (+1.14 V) and the relatively low Franck–Condon barrier associated with passage of an electron to a highly conjugated system.

Two paths are evident for reaction of $Fe(CN)_6{}^{3-}$. The $[H^+]$-proportional contribution pertains to reduction of the protonated oxidant, $[HFe(CN)_6]^{2+}$. The bimolecular rate constant for this route may, in principle, be calculated by multiplying our k_H value ($8.6 \times 10^4\ M^{-2}\ s^{-1}$) by K_A for this dipositive species. Although this K_A appears not to have been documented, it has been estimated to lie well above 0.1 [14]. A K_A value near unity (not unreasonable) then implies a rate constant near $10^5\ M^{-1}\ s^{-1}$ for the protonated path.

Reductions of the substitution-inert Ru(III) species are kinetically more complex. Rate law (5) is consistent with a competition between two reaction paths differing by a single fluoride. Both activated complexes feature, in addition to the redox partners, a unit of Ti(IV) and (from the inverse-$[H^+]$ term) the loss of a proton. If the intervention of a Ti^{II}–$Ti^{IV}(OH)$ complex is assumed, an estimate of its stability constant may be carried out by measurements at high $[Ti^{IV}]$ values, where the approach to kinetic saturation is most pronounced. Data for the 4-benzoylpyridine oxidant (Table S2) yield $K = 104 \pm 33$ for this species. Analogous treatments for the remaining Ru(III) oxidants give similar values (Table 3).

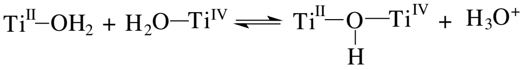
Kinetic data for reductions of Ru(III) complexes, (Tables S3–S7) when refined in terms of rate law (5), yield rate and equilibrium constants summarized in Table 3.

The modest rate increases arising from substituting keto groups or the $-CONH_2$ function on the pyridine ring are comparable to those reported for the corresponding reductions by Ti(III) [13], and many orders of magnitude less marked than those (five to seven powers of 10) in the analogous Co(III)–Cr(II) and Co(III)–Eu(II) series [15]. The very large accelerations observed in the Co^{III} systems have been taken as evidence of electron transfer via preliminary reduction of the carbonyl-bearing substituents. Here, however, we see only slight enhancements reflecting electron withdrawal from the oxidizing Ru(III) center.

The most notable feature of this study is the substantial redox catalysis by titanium(IV). This cannot reflect coordination of the Ti(IV) center to the carbonyl oxygens of the oxidants, for it remains (K_{eq} virtually unchanged) with the unsubstituted pyridine derivative.

Neither can it arise from preliminary comproportionation ($Ti^{II} + Ti^{IV} \rightarrow 2Ti^{III}$), yielding a more reactive Ti(III) species, since our Ti(II) solutions undergo no perceptible change when treated with externally prepared Ti(IV) in excess. More significantly, early measurements dealing with the reductions of these Ru(III) complexes by independently prepared Ti(III) [13] yield rates lower than our Ti(II) rates by several orders of magnitude. The close similarity among the k_1 values for the carbonyl-substituted complexes is intriguing but probably coincidental since it does not persist with the unsubstituted pyridine species.

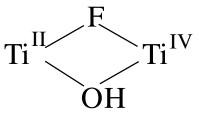
We are then dealing with a Ti(II)–Ti(IV) adduct, from which a proton has been lost (most probably from a bridging water molecule):



$$\mathrm{Ti^{II}{-}OH_2 + H_2O{-}Ti^{IV} \rightleftharpoons Ti^{II}{-}\underset{\displaystyle H}{\underset{|}{O}}{-}Ti^{IV} + H_3O^+} \qquad (6)$$

In attempting to explain the catalytic action of Ti(IV), recall that Ti(II) must be considered a sluggish reactant when its strongly negative potential is taken into account [7]. Both the $Ti(H_2O)_6^{2+}$ ($3d^2$) and the $Ti(H_2O)_6^{3+}$ ($3d^1$) cations are expected to suffer minor Jahn–Teller distortions, but the degree of such distortions and the occupancy of the non-degenerate orbitals may match poorly, resulting in slow self-exchange rate for the hexaaquated Ti(II,III) system. The loss of overall symmetry when the Ti(II) octahedron is converted to Ti^{II}–OH–Ti^{IV} may minimize structural differences between the Ti(IV)-bound divalent and trivalent states, thus lowering the Franck–Condon barrier to the redox process.

This effect may be intensified when a portion of the reductant is converted to the doubly bridged



intermediate, and the additional enhancement is reflected in the [F$^-$]-proportional kinetic term appearing in rate law (5) with all Ru(III) oxidants.

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Appendix A. Supplementary material

Tables S-1–S-7. Detailed kinetic data for redox reactions. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2007.01.026.

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